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REPLY

Response to a comment by Chun-Ming Wu on "Quantifying the tectono-metamorphic evolution of pelitic rocks from a wide range of tectonic settings: mineral compositions in equilibrium"

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Wu (2009) has commented on aspects of our paper (Caddick and Thompson 2008; hereafter CT08), whose primary purpose was to demonstrate how the coexisting compositions of minerals are highly sensitive to the available buffering assemblage in metamorphic rocks over wide ranges of pressure and temperature (*P* and *T*). The concerns of Wu involve (a) the validity of methods used to derive expressions for garnet–biotite (GB) and garnet–plagioclase (GASP) equilibria as a function of *P* and *T*, and (b) the performance of these expressions compared to alternative thermobarometer calibrations. In particular, calculation from a large thermodynamic dataset (Holland and Powell 1998) rather than a primary set of reversed equilibrium experiments, and the use of P–T–X_{Phase} relations calculated for a fixed bulk-rock composition are questioned.

CT08 examines the *P* and *T* dependence of particular exchange equilibria and net transfer (continuous) reactions using existing calibrations via published thermodynamic data and activity-composition models. Wu is correct in asserting that we have relied upon the internally consistent thermodynamic database of Holland and Powell (1998), whose work describes very clearly how they took selected experimental results into account while fitting. Using primary experimental data for calibrating mineral thermobarometers allows isolation of the mineral phases of interest, potentially improving accuracy. However, calculating phase equilibria and mineral compositions from an internally consistent dataset allows complexities arising from interaction with additional phases to be explored (if suitable mineral solution models are available). Given that the primary aim of CT08 was to demonstrate how element partitioning between commonly used thermobarometer phases can be dependent on the buffering assemblage when strongly non-ideal phases are present (e.g. CT08 Figs. 2 and 3), use of an internally consistent thermodynamic dataset was clearly required. Non-ideality of the underlying models (listed in CT08, Table 2) indeed sometimes leads to sharp deflections of $X_{\mathrm{Phase1}}/X_{\mathrm{Phase2}}$ contours when the assemblage is changed.

Wu suggests that our calculations were based solely on an average pelitic bulk-rock composition and thus loose generality. This assertion is not correct as can be seen from pages 187 to 190 of CT08. A starting pelitic bulk-rock composition was selected to present the central results, but changes to mineral compositions due to systematic variation of bulk-rock Al_2O_3, CaO and MnO were also examined (CT08 Figs. 5e/f, 6c/d and 7d). These results clearly show that the sensitivity of $\left[K_{\mathrm{D}}\right]^{\mathrm{Mg}}_{\mathrm{Fe}\,\mathrm{Gar}\,\mathrm{Bio}}$ and $\left[K_{\mathrm{N}}\right]^{\mathrm{Ca}}_{\mathrm{Gar}\,\mathrm{Plg}}$ to changing bulk-rock composition is far less than individual phase compositions (compare, for example, CT08 Fig. 6a with 6c, and Fig. 6b with 6d), suggesting that thermobarometers based upon these systems can be robust over a wide compositional range if the primary phases are suitably buffered. Demonstration over a large range of bulk-rock Al_2O_3, CaO and MnO contents reveals the limits at which $\left[K_{\mathrm{D}}\right]^{\mathrm{Mg}}_{\mathrm{Fe}\,\mathrm{Gar}\,\mathrm{Bio}}$ and $\left[K_{\mathrm{N}}\right]^{\mathrm{Ca}}_{\mathrm{Gar}\,\mathrm{Plg}}$ become strongly bulk-rock compositionally dependent (e.g. low Al_2O_3 and high *T*; CT08 Fig. 5e/f).

We agree with Wu that our expression for GB Fe–Mg exchange (Eq. 2, p. 182) fits well with the experimental data of Ferry and Spear (1978) and low temperature data of

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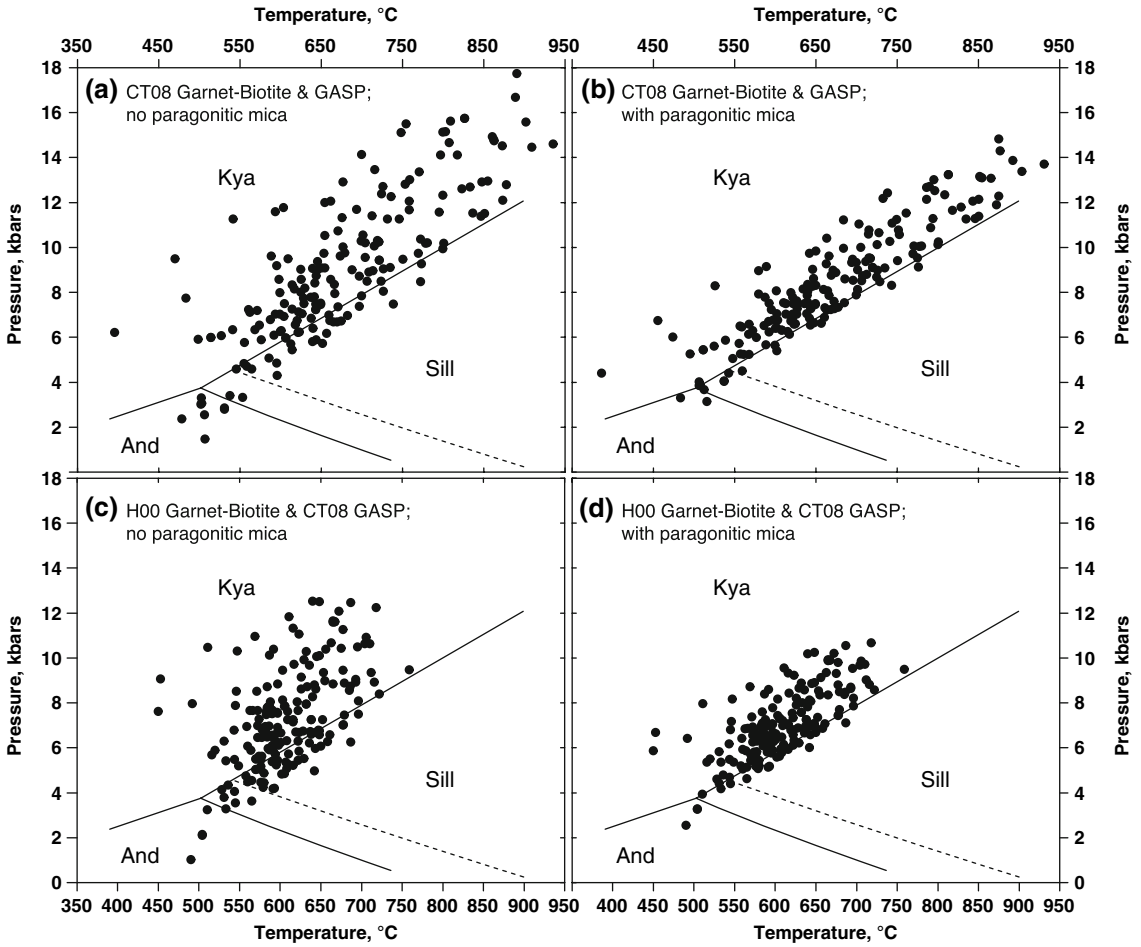

Fig. 1 *PT* conditions calculated for 185 kyanite-bearing samples collated by Wu (2009, Fig. 2) . **a**, **b** the CT08 GB-thermometer and GASP-barometer. **c**, **d** the CT08 GASP-barometer with *T* estimates from the Holdaway (2000) GB-thermomemeter (which was solved simultaneously with the Holdaway 2001 GASP barometer to independently constrain *T*). **a**, **c** consider paragonitic mica in no samples, **b**, **d** consider paragonitic mica in all samples. Al_2SiO_5 equilibria as in Wu (2009)

Perchuk and Lavrent'eva (1983), whereas it does not fit well with Perchuk and Lavrent'eva (1983) or Gessmann et al. (1997) data at high *T*. Several thermometer calibrations show similar behavior (see Wu and Cheng 2006, in particular p. 6), which here primarily reflects the choice of constraints for simultaneous fitting of the internally consistent dataset (Holland and Powell 1998, pp. 329–330). We also emphasize that our calculations were Fe^{3+} absent, and that recent solution models for biotite claim to fit high-*T* compositions far more accurately (Tajčmanová et al. 2009). We look forward to Wu's modifications of our Eq. 2 to better account for the full range of natural and experimental constraints, hopefully accounting well for the demonstrated non-ideality of mineral solutions. Further comparisons of our results with various published calibrations are available in CT08 and its supplementary material (http://www.springerlink.com/content/106416547t801868/410_2008_Article_280_ESM.html).

An alternative test for the validity of thermobarometers is to check that they yield *P–T* estimates within the correct Al_2SiO_5 polymorph stability field for Al_2SiO_5-bearing rocks (Wu 2009). Potential disequilibrium due to sluggish reaction kinetics aside, this method (see also Holdaway 2001) should allow accurate assessment of thermobarometer pairs that consistently yield unlikely equilibration conditions. Application of the GB and GASP expressions from CT08 led to 30 of 185 natural kyanite-bearing rocks plotting outside the kyanite stability field (Fig. 2b; Wu 2009). Our GASP calibration (CT08, Eq. 4) gave provision for natural assemblages containing paragonitic mica ($z = 1$) or not ($z = 0$). Wu assumes that $z = 0$ in all cases, although this is not explicitly reported with the data collated for these calculations. Although it is clear that many of these samples would not have contained appreciable Na-content in mica, recalculating *P* and *T* with $z = 1$ for all cases demonstrates the significance of this parameter (and removes several of

the 'worst' misfit *PT* points at low *T*, compare Figs. 1a, b). Following Wu's concern regarding potential accuracy of the GB thermometer, we have also recalculated pressure alone (Fig. 1c/d). Here, we used the CT08 GASP expression with temperatures calculated independently by Wu (2009) using the Holdaway (2000, 2001) thermobarometer calibrations. Again the importance of the presence or absence of paragonitic mica to the apparent pressure recovered by CT08 GASP is clear (Fig. 1c/d).

We agree with Wu (2009) that the GB and GASP expressions calibrated in CT08 are unlikely to be significantly more accurate than those calculated directly from the thermodynamic dataset. We repeat that our aim was to present bridges between thermodynamic data determined from experimental results and the very varied observations on coexisting mineral composition from natural metamorphic rocks obtained from a wide range of tectonic (*P* and *T*) settings. Wu's comment that inherited errors are rarely considered is sadly true throughout many thermobarometric studies (see discussion of Hodges and McKenna 1987). An optimum way of inferring *P* and *T* from a complex set of mineral equilibria may thus involve inverse calculation directly from internally consistent thermodynamic data, where errors can be propagated for each set of equilibria and potentially minimized by considering a larger suite of coexisting phases (e.g. Powell and Holland 2008, p. 159). All such techniques require testing and we are glad that Wu is developing such extensive databases for *PT* calibration of natural assemblages. We greet any future work that can further advance the points raised in Wu's comment.

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